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Changes in Impedance of Ni/Cd Cells With Voltage and Cycle Life

Margaret A. Reid
Lewis Research Center
Cleveland, Ohio

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CHANGES IN IMPEDANCES OF Ni/Cd CELLS WITH VOLTAGE AND CYCLE LIFE

Margaret A. Reid
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

Abstract-Impedances of aerospace design Super Ni/Cd cells arebeing measured as functions of voltage and number of cycles. The cells have been cycled over 4400 cycles to date. Analysis of the impedance data has been made using a number of equivalent circuits. The model giving the best fit over the whole range of voltage has a parallel circuit of a kinetic resistance and a constant phase element in series with the ohmic resistance. The values for the circuit elements have been treated as empirical parameters, and no attempt has been made as yet to correlate them with physical and chemical changes in the electrode. No significant changes have been seen as yet with the exception of a decrease in kinetic resistance at low states of charge in the first 500 cycles.

INTRODUCTION

As part of a long-term study of the feasibility of using impedance spectroscopy for prediction of cycle life and diagnosis of failures in space flight cells, measurements are being taken on two 19 AH aerospace design Super Ni/Cd cells. The cells are being cycled in a low earth orbit (LEO) regime to 50% state of charge (SOC). Impedances are being measured periodically at eight voltages over the entire range of state of charge. The cells have now been cycled for over 4400 cycles, equivalent to nine months in LEO. The use of sealed cells is essential in studying the effects of long-term cycling in order to avoid changes in electrolyte composition. Unfortunately, the cadmium electrode is connected to the case, so the impedances of the individual electrodes cannot be determined separately by using the case as a reference as was done earlier [1]. Parallel studies being carried out in sealed Ni/H_2 cells where the impedance is essentially that of the Ni electrode should help in assigning the contributions to the individual electrodes.

Most earlier measurements in this laboratory were made on Ni/H_2 cells and Ni electrodes at very low states of charge where the greatest differences between cells and electrodes from different manufacturers were observed. The measurements at very low frequencies (0.05 to 0.001 Hz) were the most useful. Measurements at these low frequencies and voltages are time consuming and are not suitable for routine monitoring of cells on test. One goal of the present study is to develop criteria for *monitoring cells at higher states of charge and frequencies so that it can be done routinely.*

EXPERIMENTAL

The cells are being cycled at room temperature to 50% SOC in a low earth orbit cycle consisting of a 55 minute charge and a 35 minute discharge. The charge/discharge ratio is 1.05 and the cutoff on discharge is 1.00 V. (The manufacturer, Hughes Aircraft Company, specifies that the cells should not be discharged below this except for brief periods for reconditioning).

Acceptance tests were performed at TRW before we obtained the cells. Five formation cycles were carried out upon receipt. Impedance measurements were taken then and after 100, 500, 1000, 1500, 2000, and 3000 cycles. Subsequent measurements will be taken after each 1500 cycles unless signs of failure are noted.

A Solartron 1250 FRA and 1186 Electrochemical Interface were used to take the impedance measurements, controlled by the ZPLOT computer program [2]. Measurements are made from 1000 Hz to 0.001 Hz using an AC signal of 1 mV RMS (5 mV RMS at the lowest frequencies and voltages). The data show considerable scatter at both high and low frequencies, so the automatic integration feature of the instrument is used. At high frequencies measurements are taken at each point until the standard deviation is within 1% of the average. A maximum of 200 cycles is used, which takes very little time. However, this is not true at low frequencies, so fewer cycles must be used in order to carry out the measurements in a reasonable time. At the lowest frequencies, up to eight cycles are needed to obtain satisfactory accuracy. This means that considerable time is required, up to 3-4 hours, to measure the complete frequency range at each voltage.

The measurements are initiated starting with the cell fully charged. Before making each measurement, the cells are discharged slowly to the desired voltage and equilibrated until the DC current falls to a few mA.

RESULTS AND DISCUSSION

The two cells currently being cycled have not failed (as defined by loss of 50% of capacity to a 1.0 V cutoff). One cell, however, has appeared to lose some of its capacity and was reconditioned at 3000 cycles and again after about 4400 cycles by discharging to 0.800 V instead of the usual 1.00 V. At 3000 cycles about 18% of the nominal capacity was in the second plateau and about 30% at 4400 cycles. After reconditioning, the capacity to the 1.00 V cutoff was recovered. The anticipated life is about 20,000 cycles under these conditions of temperature *and depth of discharge. Complex plane plots are shown in Figure 1 for one of the cells after 3000 cycles.*

A preliminary analysis can be made within the ZPLOT program assuming the equivalent circuit of Fig. 2a. The data are obtained by analysis of the plots generated by the program. Some typical data are given in Table I as functions of state of charge (SOC).

So far there has been little change in these parameters with cycling at the higher states of charge. At low states of charge (below 10%), the kinetic resistance and Warburg slope fell initially but have remained reasonably constant since. This can be interpreted as an initial improvement in the electrode, followed by a long period of constant behavior. No signature for prediction of end of life has been seen as yet.

This circuit, although easy to analyze, does not give a good fit to the experimental data over the whole range of voltages. In order to analyze the data further, two complex nonlinear least squares fitting programs are being used [3]. These have the capability of incorporating several additional circuit elements as well as analyzing more complex equivalent circuits. In addition, they remove the subjectivity of determining slopes and radii of circles from graphs. (All circuits discussed here include an inductance of about 7×10^{-7} Henry, which does not affect the other parameters and will not be discussed further).

Since both electrodes in the Ni/Cd cell are expected to contribute to the impedance, it would be desirable to use a circuit such as Fig. 2b or some modification of this with separate subcircuits for each electrode. The computer programs can mathematically fit the data to such models fairly well, but because we have no independent data for each electrode, i.e., no reference electrode against which to measure the impedance of each electrode separately, the parameters obtained do not follow regular trends with voltage and cycle history and thus are meaningless. Since one of the major goals of this program is to find parameters for comparison between different cells and as functions of cycling history, further work with this type of circuit was abandoned.

If we look again at circuits which lump the parameters for both electrodes into a circuit corresponding to a single electrode, we find that the circuit of Fig. 2c has been found to give the best fit at low voltages, both for Ni/H_2 cells and for Ni/Cd cells (voltages below about 1.30 V for Ni/H_2 cells and 1.26 V for Ni/Cd cells, corresponding to states of charge below about 20%). In the Ni/H_2 cell the impedance of the hydrogen electrode is negligible compared to that of the Ni electrode, so the assumption is that this essentially represents the impedance of the Ni electrode. This is probably true for Ni/Cd cells at low voltages, i.e., the impedance of the Ni electrode is apparently much larger than that of the Cd electrode so that the cell impedance again is essentially that of the Ni electrode. The second RC circuit can be interpreted as an adsorption capacitance and resistance. Unfortunately, this circuit cannot fit the data at higher voltages for either Ni/H_2 or Ni/Cd cells.

The circuit of Fig. 2d has been found to fit the data for Ni/H_2 cells satisfactorily over the whole range of voltages but cannot fit the data for Ni/Cd cells at higher voltages. This circuit incorporates a constant phase element in parallel with a resistance and a second constant phase element [3]. The combination of a constant phase element in parallel with a resistance, giving a depressed semicircle in the complex plane plot, has been interpreted as due to the fractal nature of the electrode [4]. The second constant phase element could be interpreted as simulating the Warburg diffusion.

The circuit of Fig. 2e has been the only circuit found so far that fits the experimental data for Ni/Cd cells fairly satisfactorily over the whole voltage range even though it is not quite as good at low voltages as the circuit of Fig. 2c. In addition, the values for the circuit elements follow regular trends with voltage. Thus it has been selected for detailed analysis of all of the data sets. A possible physical explanation for the components would involve an ohmic resistance plus a kinetic resistance in parallel with a diffusion element. Fig. 3 shows a comparison of the experimental and calculated complex plane plots for several data sets. The data of Figure 3b is fit better by circuit 2c, but the rest of the data is fit better by circuit 2e. Some of the values for the circuit elements are shown in Table II. The values of the ohmic and kinetic resistances and the capacitance component of the constant phase element are of the same order of magnitude as those of the first circuit, as can be seen by comparison with the data in Table I.

Some of the parameters obtained using this circuit are plotted in Figures 4, 5, and 6. The two fitting programs give almost identical results, provided that the weighing factors are the same. The trends in the parameters with cycling are similar to those found for circuit 2a, i.e., the changes in the circuit elements at any given voltage are small except for the initial increase in kinetic resistance at low voltages. The ohmic resistances have varied as the cell has cycled, but have always shown the same trends with voltage. The lower ohmic resistances for Cell 2 compared to Cell 1 in Figure 4 may be due to the fact that Cell 1 was reconditioned shortly before the measurements. There may also be some differences in the contact resistances. These aspects will be investigated further.

This circuit gives more consistent kinetic resistance and capacitance values than circuit 2a. An additional advantage of using this circuit for data analysis is that the parameters are not changed appreciably if the spectrum is only taken to 0.0025 Hz instead of 0.001 Hz. The time for taking each complete impedance spectrum is thus reduced from 3-4 hours to about one. Thus it may become feasible in the future to use impedance as a routine tool for monitoring cells for critical uses such as spacecraft if the circuit elements correlate with life and performance.

As an alternative to the usual equivalent circuits, we have done preliminary work in modeling the cell following the lead of an earlier study [5] which used mainframe circuit simulation software to define an equivalent circuit with linear and non-linear elements. We are presently using PSpice, a PC version of this software [6,7]. If this is successful, we will attempt to predict the behavior of the cell under a variety of conditions, including the transient behavior when loads are varied. This would assist in design of power systems for space applications.

Conclusion

The impedances of Super Ni/Cd cells are being studied as functions of voltage and cycle history. The data is being analyzed by several methods. The parameters determined using several simple equivalent circuits cycles have not shown any major changes during the first 3000 cycles. However, since cell failure is not expected for some time, it is not yet possible to determine whether impedance measurements will allow one to predict cell life or performance.

References

[1] M. A. Reid, *J. Power Sources* **29**, 467 (1990).

[2] L. Scribner, U. of Va., Charlottesville, VA, ZPLOT program.

[3] J. R. Macdonald, U. of North Carolina at Chapel Hill, CNLS program with shell ZSIM from L. Scribner, U. of Va, and B. Beaukamp, U. Twente, The Netherlands, EQUIVCRT program.

[4] L. Nyikos and T. Pajkossy, *Electrochim. Acta* **30**, 1533 (1985).

[5] S. Waaben, I. Moskowitz, J. Federico, and C.K. Dyer, *J. Electrochem. Soc.* **136**, 1356 (1985).

[6] J. T. Maloy and M. A. Reid, 1992 Power Sources Symposium, Cherry Hill, N.J., June 22-25, 1992.

[7] PSPICE, MicroSim Corporation, Irvine, CA 92718.

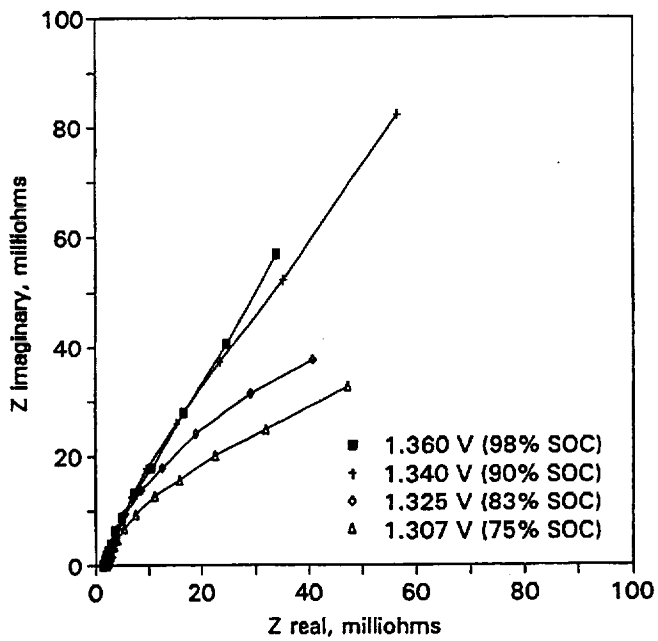
TABLES

Table I. Parameters for some of the data of Fig. 1, ZPLOT program with circuit 2a.

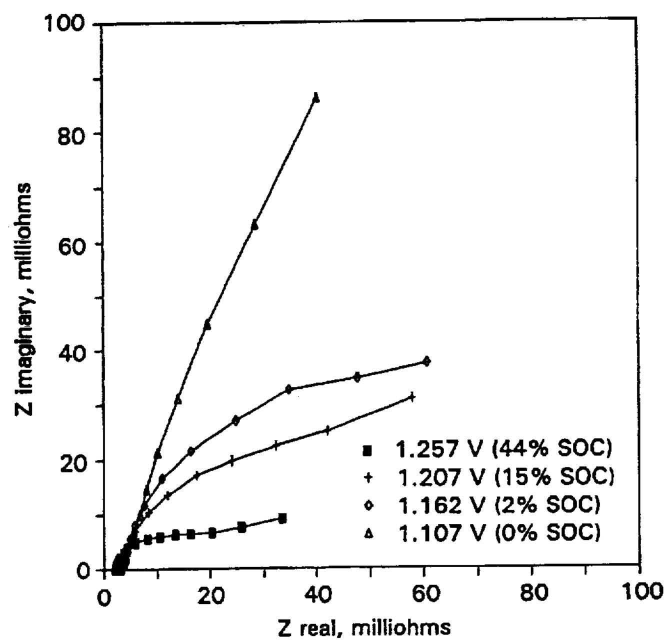
Voltage	Approx. SOC	R ohmic, mOhm	R kinetic, mOhm	Warburg Slope, mOhm $sec^{-1/2}$	Capacitance, Farads
1.360	0.98	1.44	--	3.76	1600
1.325	0.83	1.75	63	4.57	1350
1.257	0.44	2.20	14	2.64	1100
1.162	0.02	2.87	92	5.88	800

Table II. Parameters for some of the data of Fig. 1, ZFIT-CNLS program with circuit 2e.

Voltage	Approx. SOC	R ohmic, mOhm	R kinetic, mOhm	Exponent of CPE element	CPE Capacitance, Farads
1.360	0.98	1.69	252	0.815	874
1.325	0.83	1.82	102	0.817	848
1.257	0.44	2.17	34	0.690	441
1.162	0.02	2.84	101	0.795	453



(a) 1.360-1.307 V.



(b) 1.257-1.107 V.

Figure 1.—Complex plane plots for Super Ni/Cd cell #1 after 3000 LEO cycles.

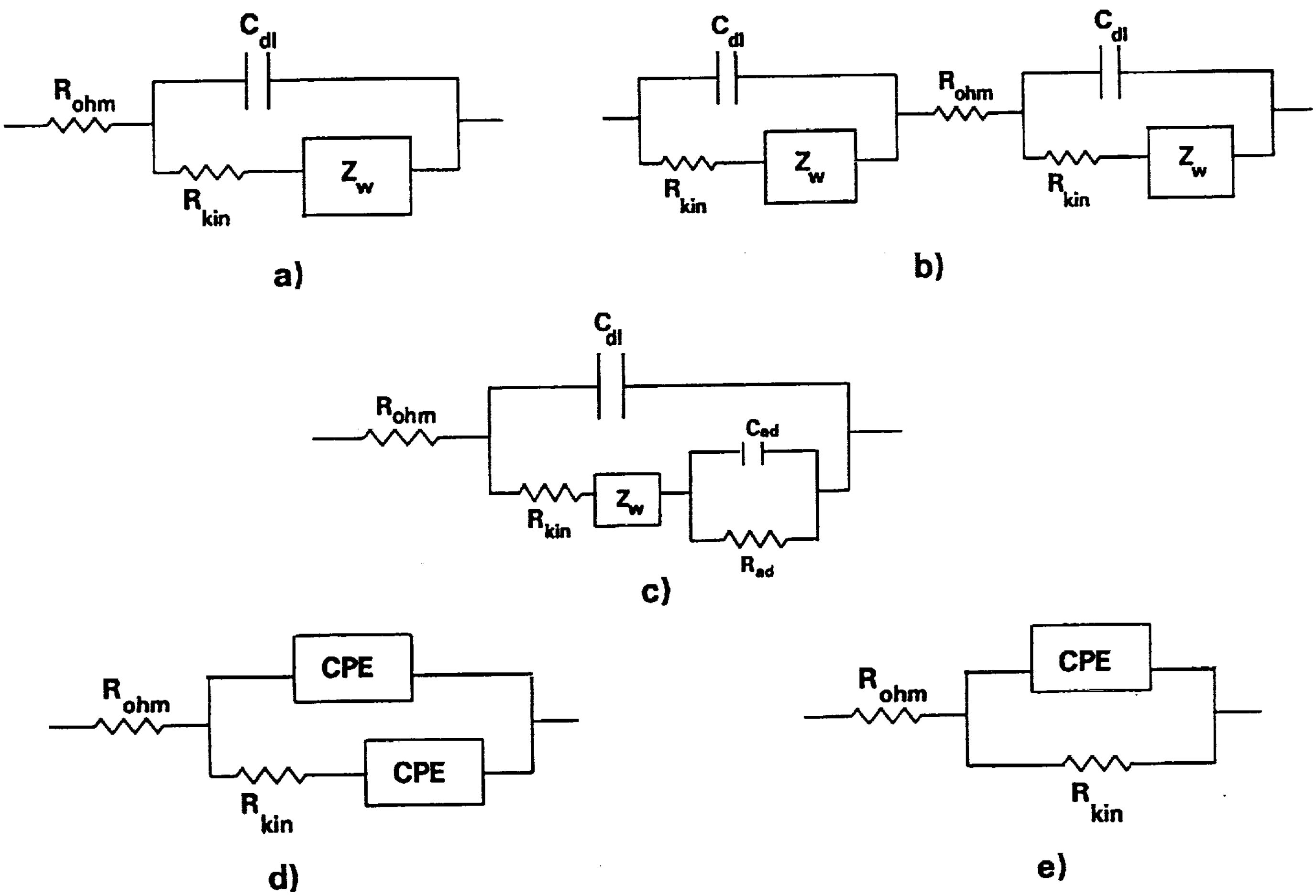


Figure 2.—Equivalent circuits used in data analysis.

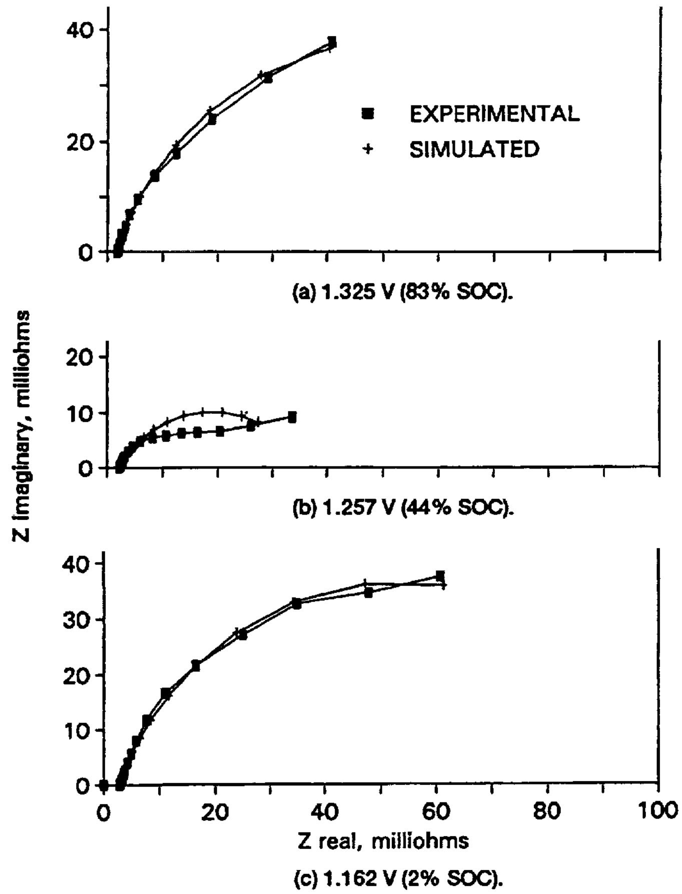


Figure 3.—Comparison of experimental and calculated complex plane plots for several data sets for cell #1 at 3000 LEO cycles using circuit 2e.

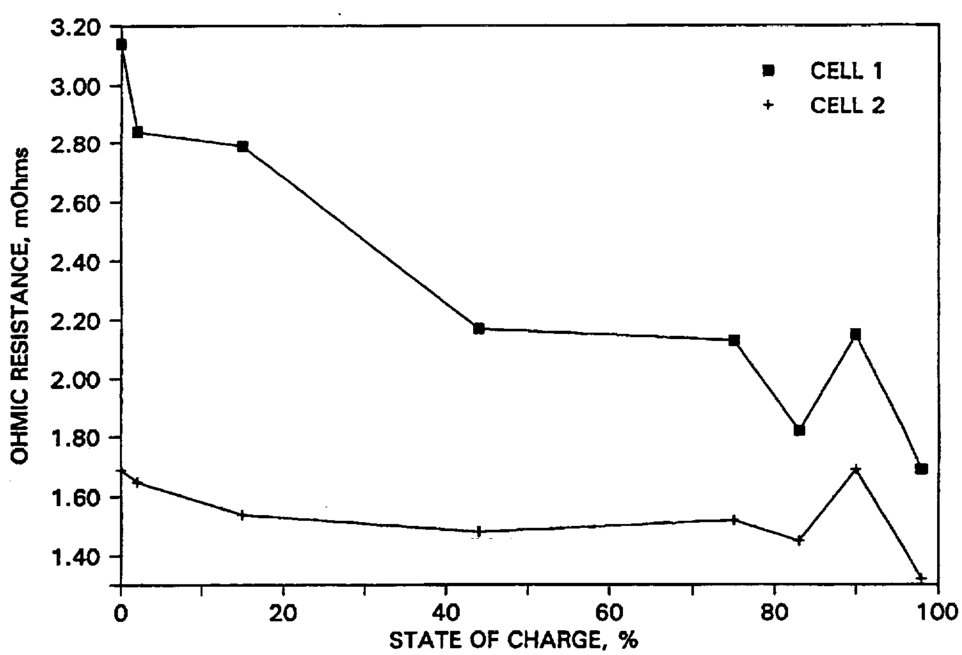


Figure 4.—Ohmic resistances versus state of charge after 3000 LEO cycles using ZSIM-CNLS program with circuit 2e.

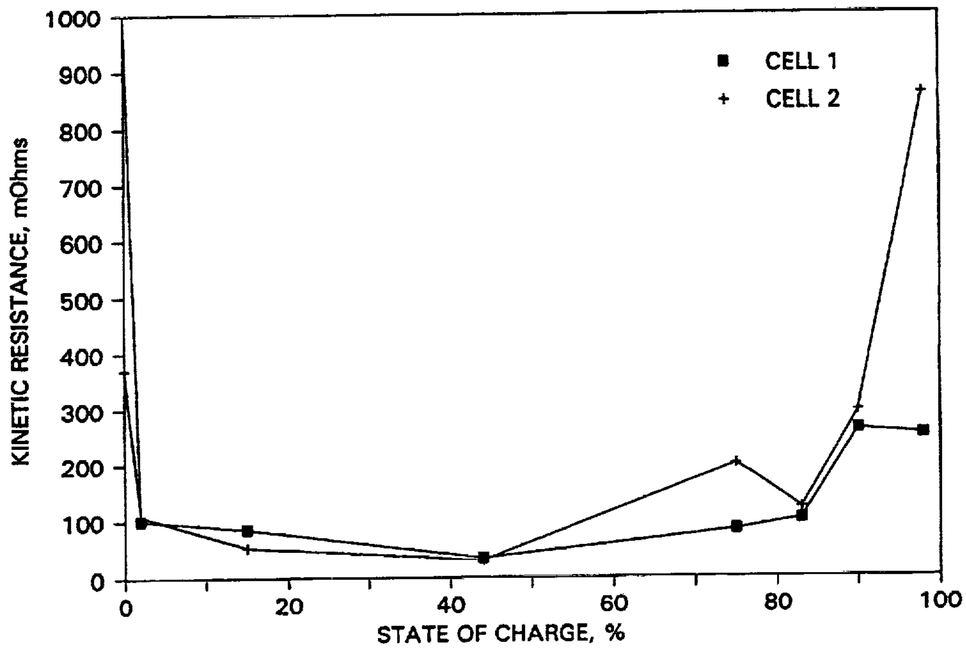


Figure 5.—Kinetic resistances versus state of charge after 3000 LEO cycles using ZSIM-CNLS program with circuit 2e.

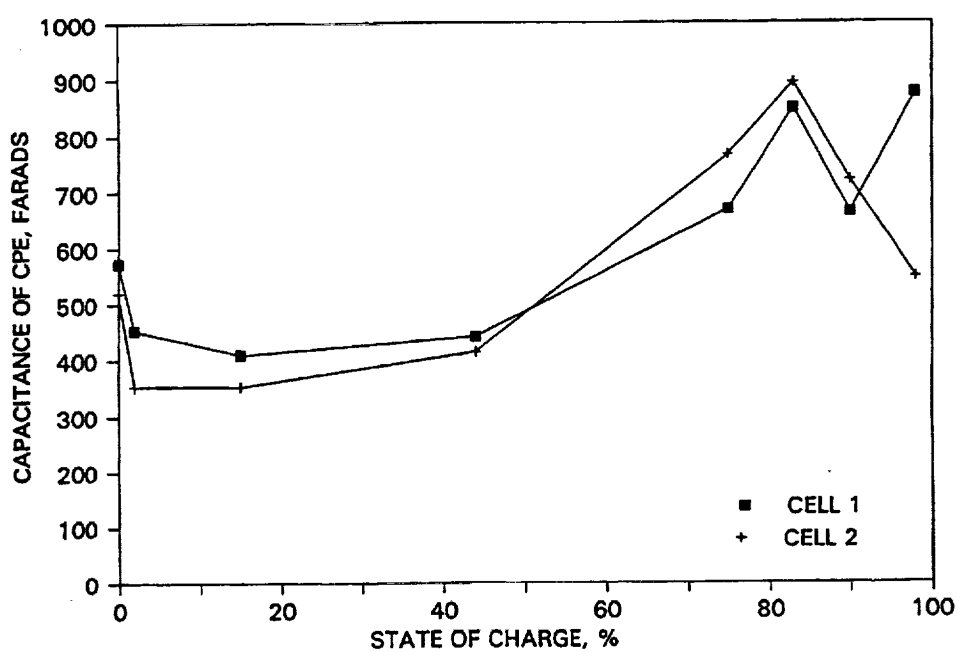


Figure 6.—Capacitance associated with CPE versus state of charge after 3000 LEO cycles using ZSIM-CNLS program with circuit 2e.

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